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Luminescence Properties of Oxyfluoride Glass and Glass-ceramic Doped with Y^{3+} Ions

L. Farahinia, M. Rezvani *

Department of Materials Science and Engineering, University of Tabriz, Tabriz, Iran

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ABSTRACT

Oxyfluoride glass- ceramics containing CaF_2 nano- crystals doped with Y^{3+} ions were prepared by one-step crystallization of SiO_2- Al_2O_3- CaO- CaF_2 glasses at different temperatures. X-ray diffraction (XRD) results have revealed that CaF_2 was the only precipitated crystalline phase in glass- ceramic samples. According to the XRD results, a glass- ceramic was selected as the best sample in order to compare its optical properties with basic glass. Photoluminescence (PL) and UV-Vis spectra are utilized to check optical properties of glass and glass- ceramic samples. A broad emission band in the visible region was determined, which was stronger in the glassy sample. Scanning electron microscopy (SEM) observation and EDX (Energy-dispersive X-ray spectroscopy) results establish the doorway of Y^{3+} ions into just some of the crystals embedded in the glassy matrix, that was the rational reason of photoluminescence intensity decrease in glass-ceramic.

1. INTRODUCTION

Although fluoride glasses are enticing materials for photonic applications due to their high transparency and low phonon energy [1-2], fabrication issues and low thermal, chemical and mechanical properties of them are undeniable [3-4]. On the other hand oxide glasses, in contrary to their high phonon energy, are additional stable and have higher mechanical properties [5-6]. Wang and Ohwaki [3] have introduced replacement transparent oxyfluoride glass- ceramics containing $Pb_xCd_{1-x}F_2$ crystals. These noble glass- ceramics offer a fluoride environment for dopants like rare- earth ions in addition to the favorable stability properties of oxide glasses [7]. Among the different fluorides, CaF_2 is more preferable due to the high transparency from 0.13 to 9.5 μm, refractive index compatibility with the aluminosilicate glass matrix and high solubility of rare-earth ions [8-10]. Therefore, rare-earth ions doped transparent oxyfluoride glass- ceramics containing CaF_2 nanocrystals have attracted abundant attention and became probable candidates for optical applications.

Different rare- earth ions are doped to those glasses and glass- ceramics with the aim of learning the luminescence and upconversion properties of them; however, to our data, there is no report of using Y^{3+} and investigating its luminescence properties. Among the various rare earth elements, yttrium has shown vital influence on optical properties of different glassy systems attributable to existence of encompassing ligand field of 4d outer-shell electrons of yttrium. In addition, reporting associate and degree uncommon and robust emission in visible region of Y^{3+} ions indifferent hosts [23, 24], which are associated with the electronic transitions within the 4d orbitals, made the authors enthusiast of studying the luminescence properties of the Y^{3+} doped oxyfluoride glass and glass- ceramic. In present study oxyfluoride glass and glass- ceramics containing CaF_2 nanocrystals doped with Y^{3+} ions were prepared successfully. Besides, luminescence behavior of both glassy and glass-ceramic samples in presence of Y^{3+} was mentioned.

2. EXPERIMENTAL PROCEDURES

The designated composition of glasses containing different amounts of Y_2O_3 (weight ratio) is given in Table 1. The mentioned composition is the most typical one, which is reported by several alternative scientists [4, 8, 11-14]. As Table 1 shows, in addition to the SiO_2, Al_2O_3 and CaF_2, the three main constituents, CaO was used. In fact, according to reaction 1, replacing some amounts of CaF_2 by CaO prevents the loss of F^- ions [15-16].

$SiO_2 + 2CaF_2 = SiF_4\uparrow + 2CaO$ (reaction 1)

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*Corresponding Author's Email: m_rezvani@tabrizu.ac.ir (M. Rezvani)

TABLE 1. Chemical composition of glasses containing different amounts of Y_2O_3 (weight ratio)

Composition (weight ratio)	SiO_2	Al_2O_3	CaO	CaF_2	Y_2O_3	As_2O_3	Sb_2O_3	K_2O
GY0.5	37.26	28.11	7.73	26.89	0.5	0.2	0.2	4.5
GY1	37.26	28.11	7.73	26.89	1	0.2	0.2	4.5
GY1.5	37.26	28.11	7.73	26.89	1.5	0.2	0.2	4.5

To obtain bubble free samples, Sb_2O_3 and As_2O_3 were used as purification agents. K_2O was applied to the batch to own appropriate melts. Different amounts of Y_2O_3 (0.5, 1 and 1.5 (weight ratio)) were added in order to introduce Y^{3+} ions. 50 g of batch was mixed and melted in alumina crucibles at 1450 °C for 1 hour in an electric furnace.

Crucibles were covered by alumina plates and quite high heating rate for melting process (15°C/min) was applied, in order to control the fluoride loss to some extent. Then preheated stainless steel molds at 500°C, were used to form the molten glass. Finally glassy discs with 0.5 cm thickness were prepared. For releasing the internal stresses of samples, annealing at 500°C for 30 min was carried out. On the basis of Differential thermal analysis (DTG- 60AH Shimadzu) results, crystallization temperatures were determined. The samples were crystallized at different temperatures ranging from crystallization peak temperature to 850°C in order to get an appropriate glass-ceramic. The precipitated crystalline phase in glass- ceramics was identified by X-ray diffraction (XRD, Siemens D-500). UV-Vis absorbance and Photoluminescence (PL) spectra of both glass and glass-ceramic samples were recorded by absorbance spectrometer (spectroscope) (UV-Vis Shimadzu 1700) and spectrofluorometer (Shimadzu RF-540), respectively. Scanning electron microscope (SEM) sample preparation consisted of polishing, etching in a 5% HF solution for 30 seconds and, applying gold-coat. At the end, SEM observation and EDX analysis of the prepared sample was carried out by Tescan MIRA3 FEG-SEM.

3. RESULT AND DISCUSSION

3.1. Differential Thermal Analysis (DTA) and choosing the Optimized Glass Sample

DTA curves with the heating rate of 10 (°C/min) for glasses with different amounts of Y_2O_3 are presented in Figure 1. In keeping with the previous reports [16-21], the appearance of two exothermic peaks in DTA results was expected. The primary peak is attributed to the crystallization of CaF_2 in several references. In contrast, there is no clear interpretation of second peak at about 900°C. Some believe that it is related to the crystallization of $CaAl_3O_6F$ [16] and a few others have not made any convincing argument on the issue [17-19]. As it is obvious in the DTA plots, the entrance of Y^{3+} ions into the glass network will increase the crystallization peak temperature of CaF_2 from 690 to 719°C. This outcome can be related to the network forming role of Y_2O_3 in glass structure. In other words, since crystallization mechanism of CaF_2 may be a three-dimensional crystal growth process controlled by the diffusion [16], more (bridging oxygen's) BOs created by Y_2O_3 dopant will increase the viscosity and consequently, decrease the mobility of ions. Thus, crystallization temperature shifts to higher temperatures.

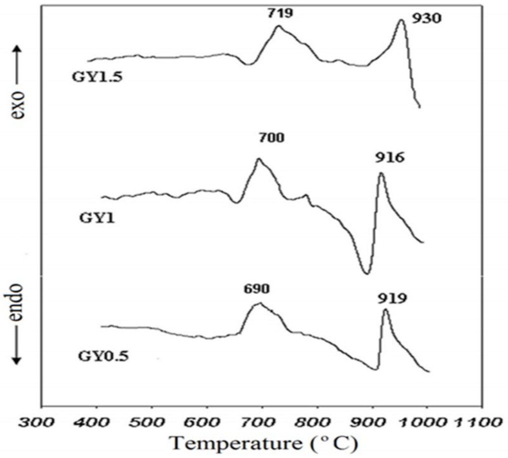
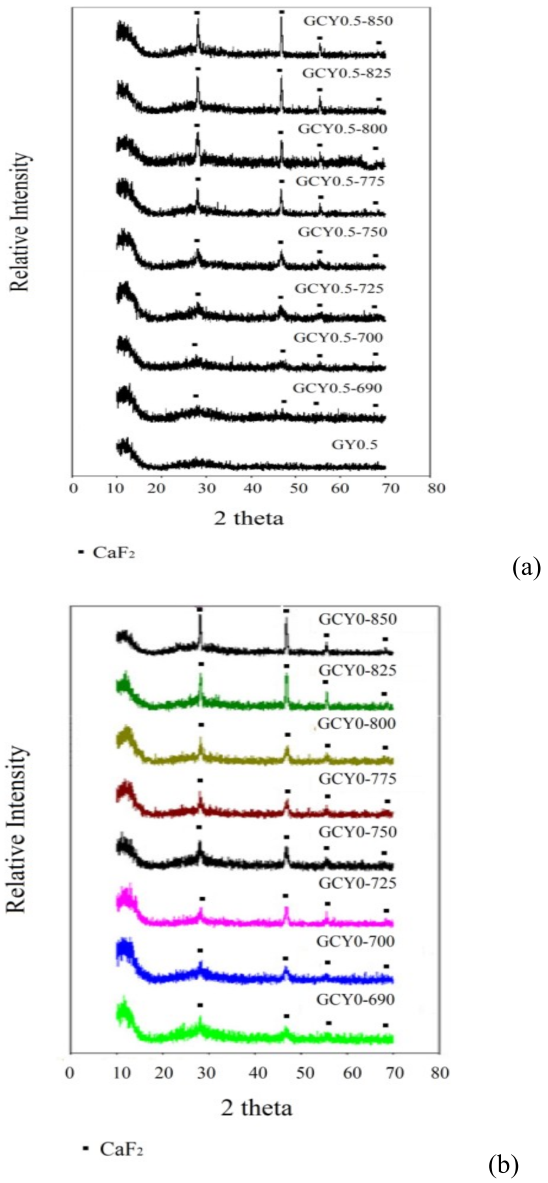


Figure 1. DTA curves of oxyfluoride glasses doped with various amounts of Y_2O_3.

On the other hand, as it will be shown in section 3.3, according to UV-Vis absorption spectra (Figure 3(a)), the absorption has increased at the side of the rise of Y_2O_3 content. One can conclude that the creation of more BOs in the glass structure prohibits the optical transmission. Considering the fact that Y_2O_3 plays a network modifier role in the structure of under- study glasses, lower crystallization temperature and higher transparency of sample containing 0.5 weight ratio, glass GY0.5 was chosen as the suitable basic glass. Therefore, with the aim of preparing glass- ceramics containing CaF_2 Nano crystals, the glass sample GY0.5 was heat treated at different temperatures ranging from the primary crystallization peak (about 690°C) to 850°C at which the glass-ceramic sample had completely lost its transparency. Crystallization conditions and crystal size of samples are tabulated in Table 2.

TABLE 2. Crystallization temperatures and crystal size of glass-ceramic samples obtained from heat-treating of glass GY0.5 with the heating rate of10 (°C/min) for 2 hours.

Sample Code	Crystallization Temperature (°C)	Crystal Size (nm)
GCY0.5-690	690	10.53
GCY0.5-700	700	15.60
GCY0.5-725	725	17.07
GCY0.5-750	750	20.39
GY0.5-775	775	33.56
GCY0.5-800	800	41.75
GCY0.5-825	825	49.09
GCY0.5-850	850	49.74



(a)

(b)

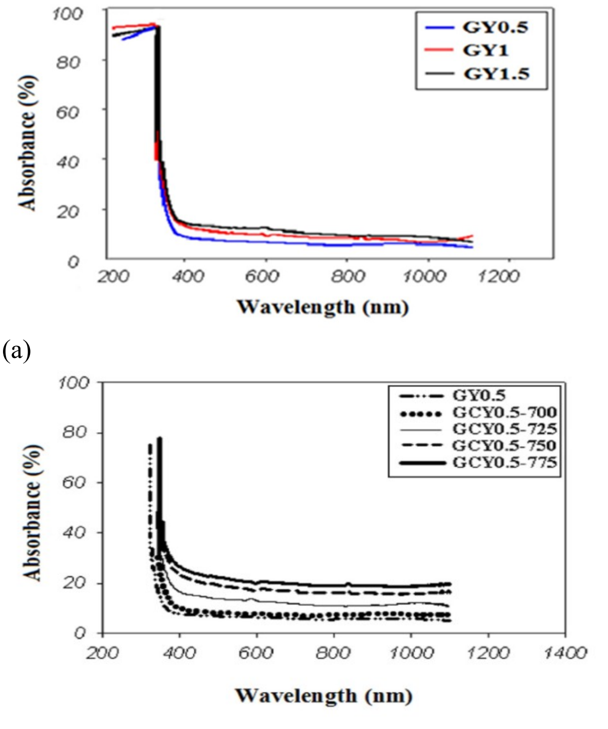
Figure 2. XRD patterns of (a) glass GY0.5 and heat treated glasses at different temperatures (b) GY0 glass heat treated at different temperatures.

3.2. X-ray diffraction (XRD) patterns

XRD patterns of the glass GY0.5 and crystallized specimens are shown in Figure 2(a). As it is illustrated in the patterns, there is no peak indicates that no unfavorable crystallization have occurred throughout the preparation of the glass. All peaks appeared in XRD patterns of crystallized samples are assigned to CaF_2 crystals (ICDD: 00-0.35-0816). Considering the crystal system of CaF2, the three main peaks of CaF2 are related to planes (111), (220) and (311), respectively. Therefore, the lattice parameter (a) of precipitated CaF_2 crystals is calculable using equation (1).

$$1/d2 = (h2 + k2 + l2) / a2 \qquad (1)$$

In order to investigate the impact of Y^{3+} ions on the lattice parameter of precipitated CaF_2 crystals, oxyfluoride glasses with no Y_2O_3 dopant (GY0) was crystallized under the similar condition of GY0.5 glass. The XRD results of the crystallized GY0 glass at different temperatures are presented in Figure 3(b).



(a)

(b)

Figure 3. (a) UV-Vis spectra of the glasses containing different amounts of Y_2O_3. (b) glass GY0.5 and glass-ceramic samples

The calculated lattice parameters are listed in Table 3. Lattice parameter of samples without Y_2O_3 dopant is extremely close to theory (0.5462 nm). Calculated lattice parameters show a rise of crystal lattice in presence of Y^{3+} ions. In conclusion, entrance of Y^{3+} ions in to CaF_2 Nano crystals is the reason of larger lattice parameter.

TABLE 3. Calculated lattice parameters for oxyfluoride glass and glass-ceramics with and without Y_2O_3 dopant

Sample Code	(hkl)	d(nm)	a(nm)
GCY0-690	(111)	0.3163	0.5480
GCY0-700		0.3165	0.5483
GCY0-725		0.3164	0.5481
GCY0-750		0.3163	0.5480
GCY0-775		0.3162	0.5479
GCY0-800		0.3166	0.5484
GCY0-825		0.3164	0.5481
GCY0-850		0.3167	0.5485
GCY0.5-690	(111)	0.3171	0.5493
GCY0.5-700		0.3171	0.5493
GCY0.5-725		0.3173	0.5496
GCY0.5-750		0.3169	0.5490
GCY0.5-775		0.3170	0.5491
GCY0.5-800		0.3171	0.5493
GCY0.5-825		0.3170	0.5491
GCY0.5-850		0.3172	0.5494

The size of CaF_2 crystals in the heat treated samples were estimated using the Scherer's equation. Among the various crystallized samples, GCY0.5-775 had acceptable transparency and crystal size (about 30nm), which make it appropriate for further analyses.

3.3. UV-Vis Spectra Figure 3(a) and (b) show the UV-Vis absorption spectra of oxyfluoride glasses with different amounts of Y_2O_3 and glass GY0.5 and some of the related glass-ceramic samples within the 300-1100 nm range, respectively. As mentioned in section 3.1. network modifier role of Y_2O_3 has decreased the transparency in samples with higher amounts of Y_2O_3.

According to Figure 3(b), attributable to the crystallization, the transparency has decreased for glass-ceramics [13]. In addition, absorption edge of glass-ceramic GCY0.5-775 is obviously shifted to longer wavelength. It may be caused by the reduction number of non- bridging fluorine (NBF) in the residual glassy phase when the CaF_2 crystalline phase precipitates [11].

3.4. Photoluminescence (PL) Study PL study was also applied to analysis the differences between the luminescence behavior of GY0.5 and GCY0.5-775. Although rare-earth ions with no 4f electrons, e.g., Y^{3+} don't have any electronic energy levels that will induce excitation and luminescence processes in or close to the visible region [22], luminescence emissions of Y^{3+} ions are reported by other researchers [23-24]. PL results of the under study samples is presented in Figure 4. which are the same as the previous reports.

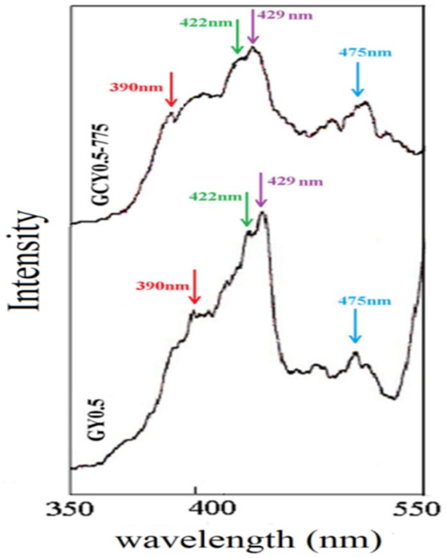


Figure 4. PL spectra of the glass GY0.5 and glass-ceramic GCY0.5-775.

Both 360 and 254nm wavelengths are used as excitation wavelengths of rare earth ions; however, in present study, because of the occurrence of luminescence emission of Y^{3+} around 420nm, the wavelength 250nm was chosen as excitation wavelength to prevent (to stop) their overlapping.

In PL spectra, it is observed two bands at about 422 and 429nm accompanied by other weaker peaks. The peaks at about 420 nm are attributed to the electronic transitions within the 4d orbitals. In other words, Y^{3+} led to the creation of secondary energy levels among the band gap and consequently emits a light in visible region [23-24].Unlike the results of other authors [25-27], glass-ceramic did not exhibit stronger emission than glass. In fact, non-controlling one-step crystallization provokes the entrance of Y^{3+} ions into just some of the CaF_2 crystals. As a consequence, throughout the PL process, Y^{3+} ions stayed in the glassy matrix are excited along with ions in crystals and because of the high phonon energy of aluminosilicate glassy matrix, the resultant emission decreases considerably.

3.5. SEM Study and EDX Analysis The SEM image of glass-ceramic GCY0.5-775 is shown in Figure 5. This image somehow confirms the entrance of Y^{3+} ions into just some crystals by depicting that some crystals are larger, i.e., the increase in size of some crystals substantiates the incorporation of dopant ions. The peak of yttrium in EDX spectra of a crystal A with larger size (Figure 6.) ascertains the incorporation of dopant ions into CaF_2 crystals, which is in agreement with XRD calculations of lattice parameter. It should be noted that appearance of weak peaks of Al and Si in EDX spectra is due to the strong effect of aluminosilicate glassy matrix.

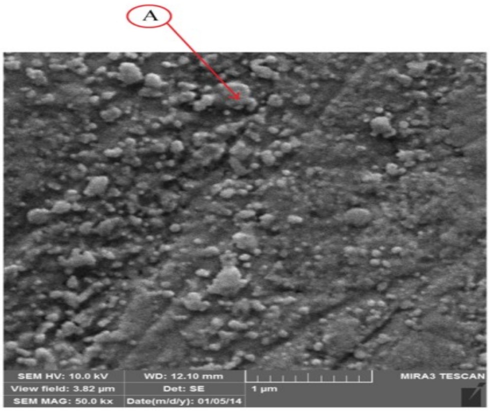


Figure 5. SEM image of glass- ceramic GCY0.5-775

4. CONCLUSIONS

In summary, Y^{3+} ions doped oxyfluoride glass was prepared by means of the common melting method. Optically transparent glass-ceramics were produced by crystallization of the GY0.5 glass at different temperatures. CaF_2 was the only crystalline phase in all of the glass-ceramics. GCY0.5-775 was selected as the best crystallized sample in order to compare with the basic glass. Both amorphous and crystallized samples showed an emission in visible range, however despite our expectation, the emission of glass-ceramic was weaker. This outcome was attributed to the entrance of Y^{3+} ions tojust some of the CaF_2 crystals embedded in the glassy matrix, which was arose from the non-controlling one-step crystallization process. Larger size of some crystals in the SEM images and results of EDX analysis confirmed the mentioned claim.

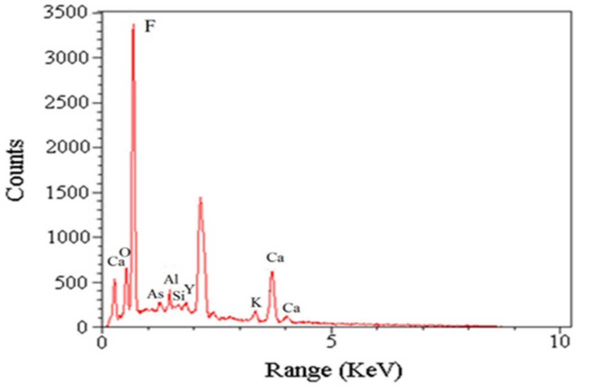


Figure 6. EDX analysis of crystal A.

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